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Cagelike Manganesilsesquioxane Complexes: Synthesis via an Acetone Approach, Structure, and Catalytic Activity for Toluene Oxidation

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Abstract

The study describes a new feature in the self-assembly of cage-like manganese-based phenylsilsesquioxanes consisting of the strong influence of acetone solvates on the formation of a cage structure. By this convenient approach, a series of new tri and tetra manganese-based silsesquioxane complexes with (i) 1,10-phenanthroline, (ii) pyrazine, or (iii) 3,5-dimethylpyrazole (dmpzH) ligands were isolated and characterized. Single-crystal X-ray diffraction studies established the molecular architectures of all of the synthesized products. Several compounds represent extraordinary types of cage-like metallasilsesquioxane (CLMS) molecular architectures. Pyrazine- and dmpzH-based Mn_3Na_3 compounds exhibit total oxidation of initial Mn(II) ions to the Mn(III) state. They present relatively weak antiferromagnetic interactions between the manganese centers. The catalytic performance of a representative precatalyst Mn-CLMS compound, $[(\text{Ph}_6\text{Si}_6\text{O}_{12})_2\text{Mn}_3\text{Na}_3(\text{dmpzH})_3(\text{acetone})_3(\text{H}_2\text{O})]$, was investigated for the microwave-assisted oxidation of toluene to obtain benzaldehyde, benzyl alcohol, and benzoic acid as the main products. The effects of reaction parameters were studied, and under optimized conditions, using the $t\text{BuOOH}$ oxidant, the oxygenated products were formed with a total yield of 54%, under microwave irradiation at 100 °C after 6 h, with 70% selectivity toward the formation of benzoic acid.

Introduction

Cage-like metallasilsesquioxanes (CLMSs) constitute a wide family of metallacomplexes, providing an impressive variety of nuclearities as well as types of molecular architectures. (1–11) These factors logically endow CLMSs with an impressive list of functions and potential applications. Among these, CLMSs' derivatives were investigated in the design of molecular magnets (including examples of single-molecule magnet or spin glass behaviors) (12–18) and objects with photophysical properties (e.g., CLMS-based luminescent thermometers). (19–22) In turn, several functional coordination polymers, (23–26) ceramics, (27,28) anodes, (29,30) fungicides, (31) and flame retardants (32) were successfully developed on the basis of CLMSs. CLMSs are widely applied as homo- and heterogeneous catalysts as well as components of catalytic systems. (28,33–39) Among recent reports, CLMSs' activity in (i) deacetalization/deketalization-Knoevenagel reactions, (40) (ii) Chan–Evans–Lam couplings, (41) (iii) Baeyer–Villiger reactions, (42) (iv) CO_2 valorization, (31,43) and (v) carboxylations (44) should be mentioned. Intriguingly, despite detailed investigations of Mn complexes in catalysis, (45,46) the very first example of catalytically active Mn-CLMSs has been reported by some of us very recently for the oxidative

amidation conditions. (47) In turn, Mn–CLMSs remain as not widespread representatives of the metallasilsesquioxanes family (only six examples were described before 2021), even though impressive molecular architectures are characteristic of these compounds. (15,48–53) Being interested in both directions, (i) molecular design of Mn–CLMSs and (ii) evaluation of their catalytic properties, we developed an original “acetone-driven” approach to a new family of Mn–CLMS complexes.

Toluene is a common aromatic volatile organic compound (VOC) that is of particular interest due to its widespread utilization in several chemical industries, such as solvent production, paint manufacturing, pharmaceuticals, and combustion fuel blending. (54–57) It is also associated with significant health hazards and environmental concerns. (58,59)

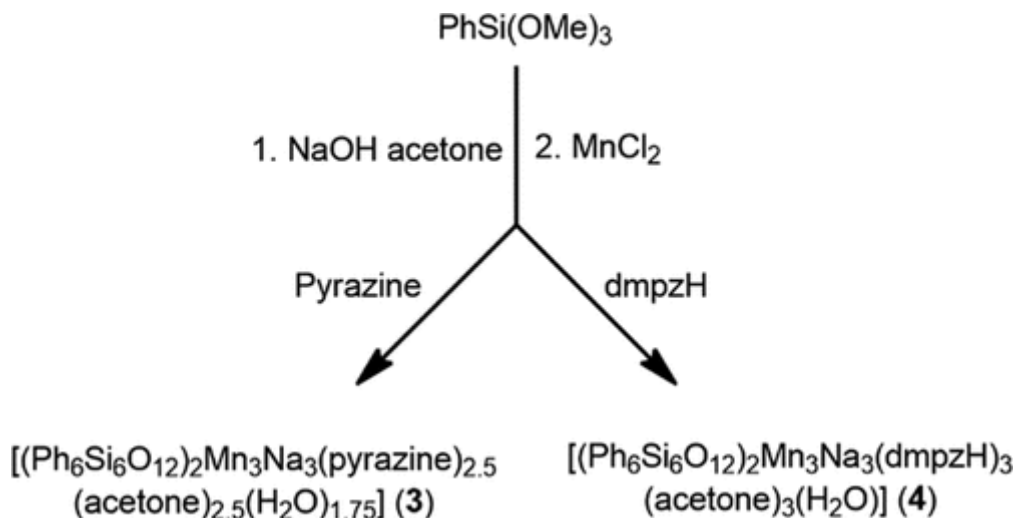
The catalytic oxidation of toluene represents a promising approach for its transformation into value-added products, including benzaldehyde, benzyl alcohol, cresols, and benzoic acid, thereby reducing its environmental footprint. (60–62) These oxygenated products have various applications in many chemical industries, serving as intermediates for the synthesis of pharmaceuticals, fragrances, and polymers. (63–66) Therefore, developing efficient and selective catalytic systems for toluene oxidation is of great interest from both environmental and economic standpoints.

Significant progress has been made in the field of homogeneous catalytic oxidation of toluene using various abundant first-row transition metal catalysts that show promising catalytic activities. (67–73) Manganese-based catalysts have gained considerable attention due to the high natural abundance and varied oxidation states (–3 to +7) of this metal. (45,74–76) Although hydrocarbon catalytic oxidation reactions based on Mn complexes have been intensively studied, (77–84) their utilization for homogeneous oxidation of toluene is still very scarce. (85)

Following our interest in the mild oxidation of hydrocarbon VOCs, a representative Mn_3Na_3 -based compound was employed as a catalyst for the microwave-assisted homogeneous oxidation of toluene as a model substrate, making it the first example of CLMS exhibiting catalytic activity toward this particular reaction.

Results and Discussion

Synthesis and Structure



Scheme 1. General Method of the Synthesis of Mn_3Na_3 –Phenylsilsesquioxane Complexes with Pyrazine **3** and dmpzH **4**.

A choice of fruitful synthetic solutions for the self-assembly of CLMS complexes remains a challenging task. Numerous articles confirm the opportunity for transformation of simple RSi(OR')_3 reagents into complicated CLMS structures (14–18,20–26,41–44,86,87) via the intermediate alkaline hydrolysis stage. (88,89) In this context, recent positive results witnessed a successful approach to a large family (14 examples) of copper-based CLMSs via the use of acetone as a key solvate. (21,23,90) To reveal the reproducibility of the “acetone principle” on Mn–CLMSs self-assembly, we performed the synthesis of two analogues of compounds from ref (47) in the presence of acetone (Scheme S1). They successfully provided the compounds $[(\text{Ph}_6\text{Si}_6\text{O}_{12})_2\text{Mn}_3^{\text{III}}\text{Mn}^{\text{II}}\text{Na}_2\text{Cl}(\text{phen})(\text{DMF})_4(\text{acetone})]$. 2(acetone) **1** in 69% yield (Figure S1) and $[(\text{Ph}_4\text{Si}_4\text{O}_8)_2\text{Mn}_2^{\text{III}}\text{Mn}_2^{\text{II}}(\text{OH})_2(\text{phen})_4]$. 5.5(acetone) **2** in 50% yield (Figure S2). The structures of both compounds **1** and **2** are similar to those of their predecessors and thus discussed in the SI. Higher yields of **1** and **2** than those for complexes reported in ref (47) (69 vs 60%, 50 vs 39%) pointed out the potential of acetone as a key solvating ligand. In the progress of this approach, we performed the self-assembly synthesis of Mn–silsesquioxanes in acetone media. As the formation of single-crystal products directly from the initial reaction media was found unsuccessful, additional complexations with pyrazine (Scheme 1, left) and 3,5-dimethylpyrazole (dmpzH; Scheme 1, right) were performed. Both reactions smoothly gave cage compounds, namely,

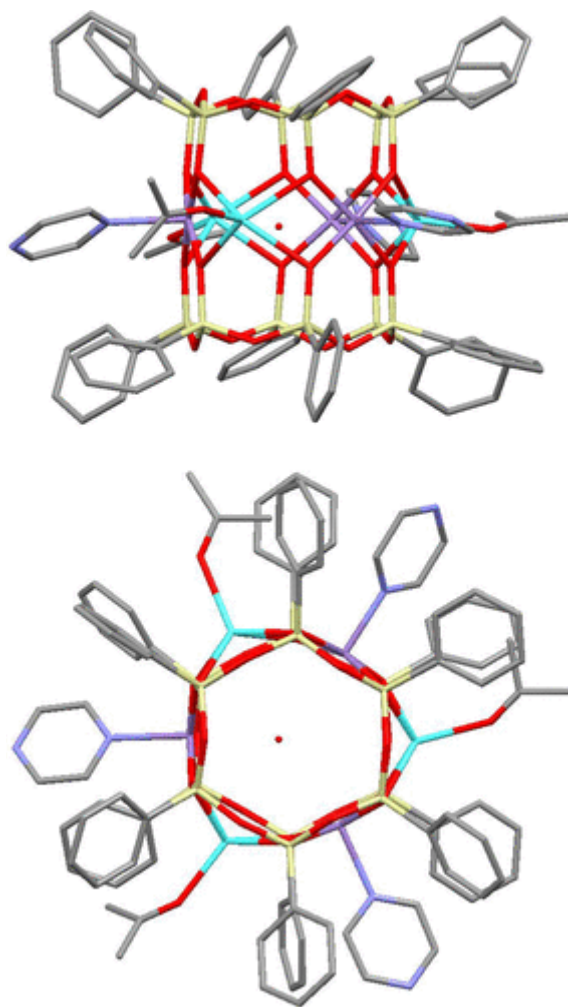


Figure 1. Side and top views of the Mn_3Na_3 –phenylsilsesquioxane complex with pyrazine ligand **3**. Color code: Si, yellow; O, red; Mn, violet; Na, aquamarine; C, gray; N, blue.

$[(\text{Ph}_6\text{Si}_6\text{O}_{12})_2\text{Mn}_3^{\text{III}}\text{Na}_3(\text{pyrazine})_{2.5}(\text{acetone})_{2.5}(\text{H}_2\text{O})_{1.75}]$ **3** (in 58% yield) and $[(\text{Ph}_6\text{Si}_6\text{O}_{12})_2\text{Mn}_3^{\text{III}}\text{Na}_3(\text{dmpzH})_3(\text{acetone})_3(\text{H}_2\text{O})]$ **4** (in 64% yield).

Several structural features of compounds **3** and **4** (Figures 1 and 2) are unprecedented for the CLMS family. First of all, this type of nuclearity (Mn_3Na_3) has never been reported for Mn–CLMSs. Second, sodium cations are intriguingly located, along with the transition metal ions, in the metal belt of prismatic CLMSs. Repeating $\text{Mn}\cdots\text{O}\cdots\text{Na}$ contacts form a distorted circular central unit (Figure 3). Such a location of metal ions allowed each manganese ion to be coordinated by an organic ligand (pyrazine for **3**; 3,5-dimethylpyrazole for **4**). At the same time, the sodium centers of **3** and **4**, despite their location in the same basal plane with manganese centers, remain “ligand-naked.” It is interesting to compare this feature with other types of “ligand-rich” CLMSs: Cu_4Na_4 –

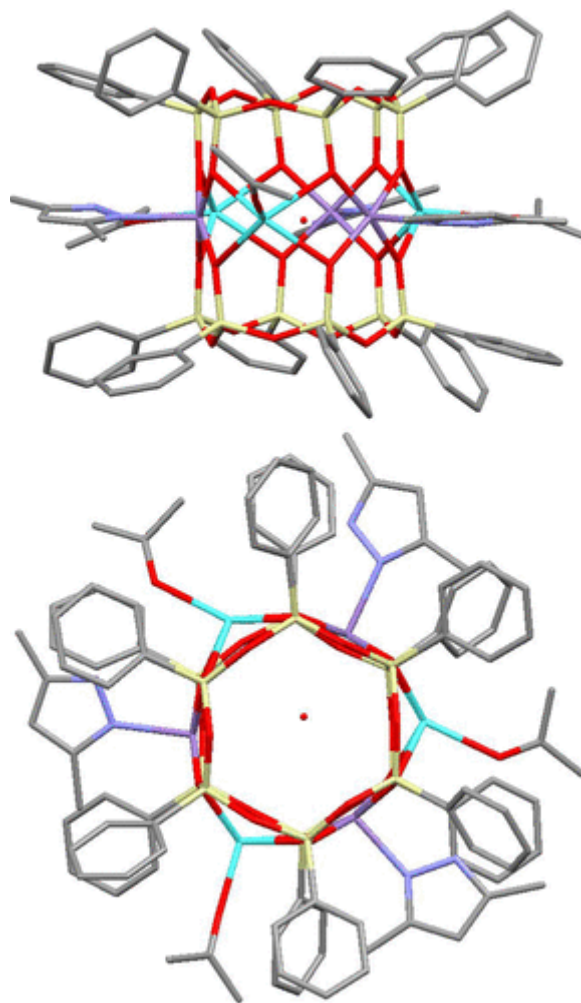


Figure 2. Side and top views of the Mn_3Na_3 -phenylsilsesquioxane complex with dmpzH ligand **4**. Color code is the same as that for Figure 1.

CLMS represents an inverse type of ligation, where sodium centers are ligated by phenanthrolines, while copper ions are “ligand-naked.” (91)

Two additional structural features should be mentioned in the context of *N,N*-ligands in the structures of **3** and **4**. For complex **3**, one could see that despite the strong tendency of pyrazine to bridge metal ions, (92) it coordinates only to the manganese center of one cage without formation of a coordination polymer structure. This is quite unusual in comparison to the well-described ability of 1,4-dioxane (which could be considered as a pyrazine structural analogue) to form CLMSs’ supramolecular assemblies. (16,91,93,94) For complex **4**, one can observe a simple, pyridine-like coordination of a dmpzH ligand to the manganese center. Thus, no tendency of the pyrazole ligand to bind in an endo- or exobidentate fashion (95) is detected here. This is also unusual, taking in

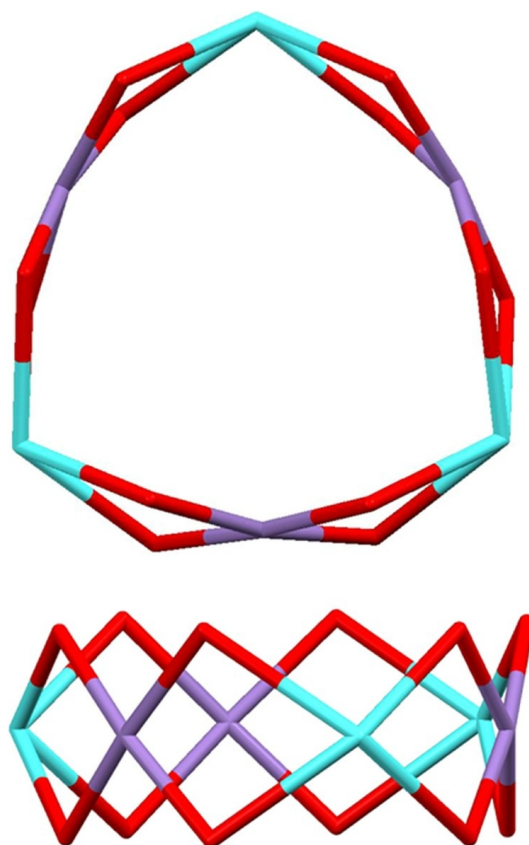


Figure 3. Two projections of the metal oxide central belt in complexes **3-4**. Color code is the same as that for Figure 1. Encapsulated water molecules are not shown.

mind the fact that all previously reported examples of pyrazolate-involved metallasesquioxanes described a bridging manner of ligation. (21,43,96,97)

Finally, the formation of compounds **3** and **4** involves the spontaneous oxidation of initial Mn^{II} ions (from the MnCl_2 reagent). Several previous reports on Mn-CLMSs discussed only partial oxidation of manganese(II) to manganese(III) with the formation of mixed $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}$ -CLMSs, (15,47,53) including compounds **1** and **2**. Unlike this, all manganese ions in **3** and **4** are in the $\text{Mn}(\text{III})$ state, giving nine positive charges. With three positive charges from three sodium ions, this is enough to compensate for 12 negative charges from two hexameric silsesquioxane ligands $(\text{Ph}_6\text{Si}_6\text{O}_{12})^{6-}$. Finally, one can see encapsulated species (water molecule) in the inner cavity of both cages in **3** and **4**. This can be compared to the observation of an encapsulated chloride in a sandwich-like Mn_6 -silsesquioxane. (48) Both compounds **3** and **4** exhibit the presence of d-d transitions (ultraviolet-visible (UV-vis) spectra, Figure S4) and a similar set of peaks in IR spectra (Figure S5): $1700\text{--}1550\text{ cm}^{-1}$ ($\nu\text{C}=\text{C}$, $\nu\text{C}=\text{N}$), 1150 cm^{-1} ($\nu\text{Ph-Si}$), $1050\text{--}940\text{ cm}^{-1}$ ($\nu\text{asSi-O}$, $\nu\text{asSi-O-Si}$), 900 cm^{-1}

(vasSi–O in the Si–O–M fragment), and 730–670 cm^{-1} ($\sigma\text{C–H}$ of the monosubstituted phenyl group). These characteristics are quite usual for the CLMS family.

Magnetic Properties

The magnetic properties of compounds **3** and **4** were investigated with a SQUID MPMS3 magnetometer working in the 1.8–310 K range up to 7 T. The temperature dependences of the magnetic susceptibility in direct current (dc) mode were performed under an applied magnetic field of 1000 Oe. At room temperature, the χT values of 8.25 and 10 $\text{cm}^3 \text{K mol}^{-1}$ for **3** and **4**, respectively, are in a relatively good agreement with the theoretical value of 9.0 $\text{cm}^3 \text{K mol}^{-1}$ expected for three noninteracting Mn^{3+} ions assuming an isotropic g -value of 2.00. (98,99) For both compounds, the χT product decreases as the temperature decreases, which reflects the presence of antiferromagnetic interactions between the manganese ions or zero-field splitting (Figure 4a).

The field dependences of the magnetization performed at 1.8 K for both compounds show a linear and rapid increase of magnetization in the low field region and then a slow increase after 1 T. However, saturation is never reached even at 7 T, which indicates the presence of antiferromagnetic interactions.

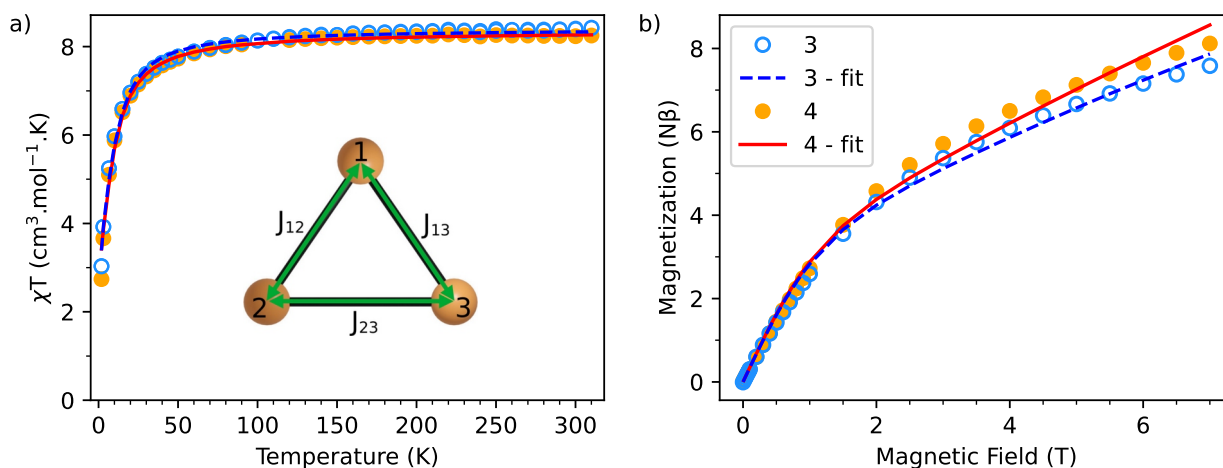


Figure 4. (a) χT curves under an external magnetic field of 1000 Oe as a function of temperature for **3** and **4**. Inset: schematic representation of the triangle with a nonequivalent exchange path in **3** and **4** with three different interactions between Mn^{3+} ions (J_{12} , J_{13} , and J_{23}) used for the fit. (b) Magnetization curves at 1.8 K as a function of the external continuous magnetic field for **3** and **4**. The circle symbols represent the experimental data, and the line curves represent the fit using Hamiltonian (1).

The magnetic data were fitted by using isotropic Heisenberg interactions on the triangle with three nonequivalent exchange paths in the structure (see the inset in Figure 4a) following PHI Chilton's group software (100)

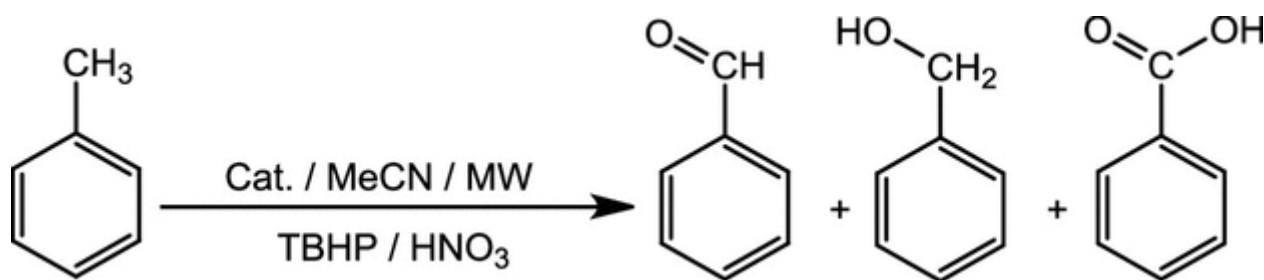
$$\mathcal{H} = \mu_B g \sum_{i=1}^N \vec{S}_i \cdot \vec{B} - 2 \sum_{i < j}^{i,j \in N} J_{ij} (\vec{S}_i \cdot \vec{S}_j) \quad (1)$$

where \vec{S}_i is the spin of the i th ion, \vec{B} is the external magnetic field, g is the g -factor, and J_{ij} is the magnetic exchange energy between the i th and j th ions. The best obtained parameters are equal to $J_{12} = -1.51 \pm 0.02$, $J_{13} = 0.63 \pm 0.02$, and $J_{23} = 0.24 \pm 0.01 \text{ cm}^{-1}$ with $g = 1.932 \pm 0.001$ for **3** and $J_{12} = -1.17 \pm 0.01$, $J_{13} = 0.20 \pm 0.04$, and $J_{23} = 0.11 \pm 0.02 \text{ cm}^{-1}$ with $g = 1.927 \pm 0.001$ for **4**. Note that the obtained interactions are rather weak, as expected considering the relatively long intramolecular distances between the manganese atoms in the structure (for instance, direct intramolecular Mn...Mn distances vary between 4.995 and 5.069 Å for **3** and between 4.911 and 4.997 Å for **4**).

Catalytic Properties

The catalytic performance of compound **4** was evaluated for the oxidation of aromatic VOCs to produce valuable oxygenated products, and toluene was chosen as the representative substrate due to its significant potential health and environmental risks. (58,59) Under microwave irradiation, compound **4** demonstrated a catalytic activity in the peroxidative oxidation of toluene using an aqueous solution of $t\text{BuOOH}$ (TBHP) in acetonitrile in the presence of nitric acid as a cocatalyst, which resulted in the formation of benzaldehyde, benzyl alcohol, and benzoic acid (Table 1). TBHP was selected as an environmentally friendly oxidizing agent, comparable to hydrogen peroxide (H_2O_2) and molecular oxygen (O_2), due to its higher reactivity in comparison to O_2 and greater thermal stability than H_2O_2 . (101) Furthermore, TBHP could be conveniently employed as an oxidizing agent in a closed vial under microwave irradiation. (84,102,103) Acetonitrile was chosen as the preferred solvent for its resistance to oxidation under the experimental conditions employed in this study and its ability to activate peroxides by forming the peroxyimide intermediate, which acts as an effective oxygen transfer agent. (104)

To investigate the effect of the catalyst loading, the reactions were typically conducted in the presence of 0.4 mmol of toluene, 1.2 mmol (3 equiv) of the TBHP oxidant, and nitric acid

Table 1. Toluene Oxidation Using Catalyst **4**^a

entry	catalyst loading ^b (mol %)	oxidant ^b (n equiv)	acid/catalyst	temperature (°C)	time (h)	yield (%) ^c			
						benzaldehyde	benzyl alcohol	benzoic acid	total
1	0.25	3	50	80	1	11.6	4.0	3.5	19.1
2	0.5	3	50	80	1	6.6	2.0	4.3	12.9
3	3	3	50	80	1	5.9	2.4	2.6	10.9
4 ^d	0.5	3	50	80	12	5.6	2.1	5.6	13.4
5	0.5	1	50	80	1	5.8	2.4	3.3	11.5
6	0.5	5	50	80	1	7.3	2.0	3.2	12.5
7	0.5	10	50	80	1	8.5	1.7	2.0	12.2
8	0.5	3	10	80	1	4.2	1.1	3.0	8.3
9	0.5	3	30	80	1	6.4	2.0	3.9	12.3
10	0.5	3	90	80	1	6.7	2.1	4.0	12.8
11	0.5	3	50	80	3	6.8	2.2	10.1	19.1
12	0.5	3	50	80	6	11.7	4.4	26.4	42.5
13	0.5	3	50	80	8	11.9	4.0	28.1	44.0
14	0.5	3	50	60	1	7.1	1.6	0	8.7
15	0.5	3	50	100	1	7.5	2.1	10.9	20.5
16 ^e	0.5	3	50	100	1	6.3	0	3.9	10.2
17 ^f	0.5	3	50	80	1	5.2	0	3.3	8.5
18 ^g	0.5	3	50	80	1	3.7	0	0	3.7
19 ^h	0.5	3	50	80	1	4.9	1.5	0	6.4
20	0.5	3	50	100	6	12.2	4.6	36.8	53.6
21 ⁱ	0.5	3	50	100	6	3.4	0	3.6	7.0

^aReaction conditions: toluene (0.4 mmol), catalyst **4**, aqueous TBHP (70%), 350 μ L of the MeCN solvent, nitric acid, MW irradiation (10 W).

^bBased on toluene.

^cDetermined by GC analysis.

^dReaction performed under conventional heating in an oil bath.

^eReaction performed in a mixture of H₂O and MeCN (1:4). ^fReaction performed in a mixture of H₂O and MeCN (1:1).

^gReaction performed in H₂O as a sole solvent.

^hReaction performed using MnCl₂ as a catalyst. ⁱReaction performed in the presence of diphenylamine.

(acid/catalyst ratio of 50) in acetonitrile at 80 °C under microwave irradiation for 1 h. Increasing the catalyst amount from 0.25 to 3 mol % had a negative impact on the total yield, which decreased from 19 to 11%, and the amount of benzaldehyde obtained (Table 1, entries 1–3, and Figure 5). However, the highest yield of benzoic acid was observed using 0.5 mol % of the catalyst.

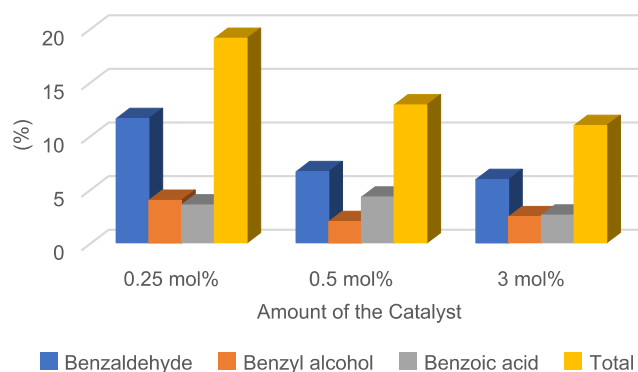


Figure 5. Yields obtained from the toluene oxidation reaction using different amounts of catalyst **4**. {Reaction conditions: toluene (0.4 mmol), TBHP (1.12 mmol), MeCN (350 μ L), HNO₃ (Acid/Cat. = 50), 80 $^{\circ}$ C, 1 h}.

To study the effect of microwave irradiation as a more efficient energy source, the reaction was conducted using a 0.5 mol % catalyst under conventional heating in an oil bath at 80 $^{\circ}$ C (Table 1, entry 4). The mixture of the oxidized products was obtained in a total yield of 13.4% after 12 h, which is comparable to that obtained after only 1 h under microwave irradiation (Table 1, entry 2). Considering the evident time efficiency advantage associated with microwave utilization, it will be used as the energy source for the rest of the study.

Increasing the amount of the TBHP oxidant from 1- to 10-fold molar equivalents, relative to the substrate, had no effect on the total yield, which remained around 12% without a significant change (Table 1, entries 2 and 5–7, and Figure 6), agreeing with the robust nature of the catalyst and the stability of the catalytic species in harsh oxidizing conditions. However, it did improve the selectivity toward benzaldehyde formation and reduced benzoic acid amounts. The maximum quantity of benzoic acid was obtained when using a toluene-to-oxidant ratio of 1:3.

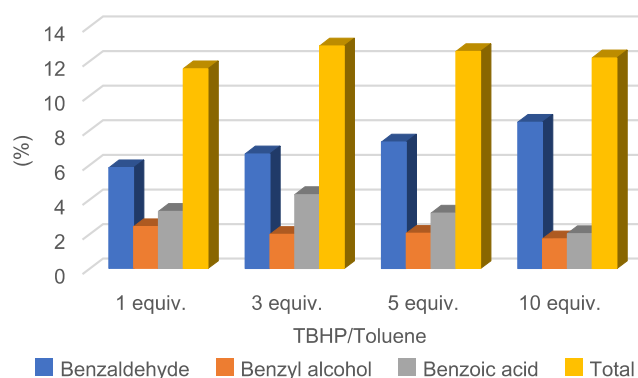


Figure 6. Yields obtained from the toluene oxidation reaction using different amounts of the TBHP oxidant. {Reaction conditions: toluene (0.4 mmol), catalyst (0.5 mol %), MeCN (350 μ L), HNO₃ (Acid/Cat. = 50), 80 $^{\circ}$ C, 1 h}.

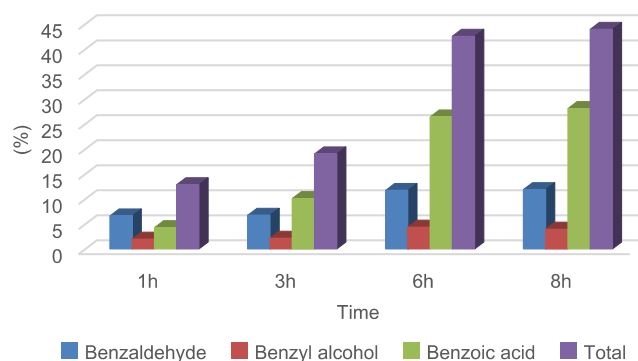


Figure 7. Yields obtained from the toluene oxidation reaction using catalyst **4** to study the effect of reaction time. {Reaction conditions: toluene (0.4 mmol), catalysts (0.5 mol %), TBHP (1.12 mmol), MeCN (350 μ L), HNO₃ (Acid/Cat. = 50), 80 $^{\circ}$ C}.

Enhancing the nitric acid-to-catalyst **4** ratio from 10 to 30 in the reaction medium improved the reaction rate by increasing the yield of all three oxidation products (Table 1, entries 2 and 8–10). However, further increasing the amount of the acid cocatalyst did not have a significant effect on either the total reaction yield or selectivity toward a specific product.

Increasing the reaction time from 1 to 6 h promoted the production of all of the oxygenated products, with the overall yield increasing from 12.9 to 42.5%, and improved the selectivity toward benzoic acid formation from 33.3 to 62.1% (Table 1, entries 2 and 11–13, and Figure 7). Extending the reaction time to 8 h only slightly increased the total yield from 42.5 to 44%.

The effect of the temperature parameter has also been studied (Table 1, entries 2, 14, and 15, and Figure 8). Increasing the reaction temperature from 60 to 100 $^{\circ}$ C did not have a considerable effect on the amounts of benzaldehyde and benzyl alcohol obtained. However, the quantities of benzoic acid formed were improved, resulting in an overall increase in the total yield.

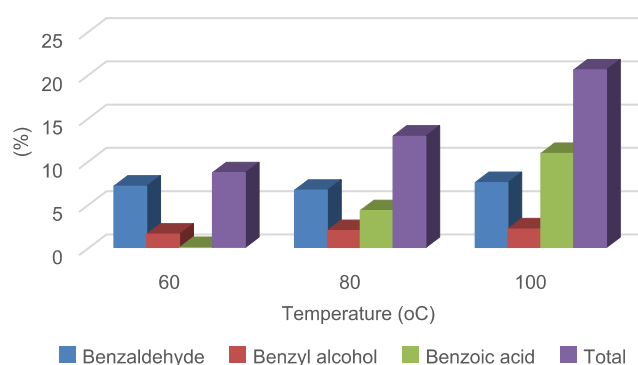


Figure 8. Yields obtained from the toluene oxidation reaction using catalyst **4** to study the effect of reaction temperature. {Reaction conditions: toluene (0.4 mmol), catalysts (0.5 mol %), TBHP (1.12 mmol), MeCN (350 μ L), HNO₃ (Acid/Cat. = 50), 1 h}.

Due to the utilization of aqueous TBHP solution as an oxidant, water is already present in the reaction medium. To investigate the impact of water content on the reaction progress, additional experiments were performed by introducing further water amounts in the reaction medium (Table 1, entries 2 and 16–18, and Figure 9). It was observed that increasing the amounts of water in the reaction medium had a negative impact on the total yield of the oxygenated products. However, the selectivity toward benzaldehyde formation increased from 51.5%, without additional amounts of water, to 100% when water was employed as the sole solvent.

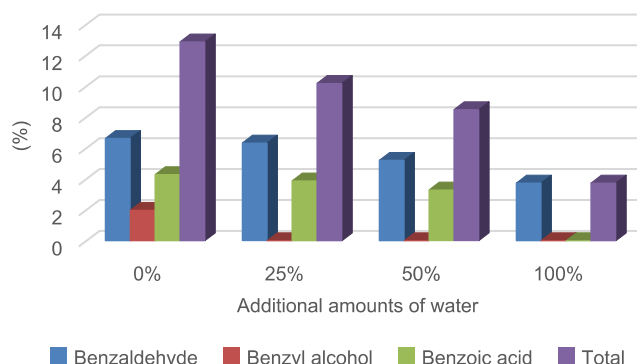


Figure 9. Yields obtained from the toluene oxidation reaction using catalyst **4** to study the effect of using additional water amounts. {Reaction conditions: toluene (0.4 mmol), catalysts (0.5 mol %), TBHP (1.12 mmol), MeCN + H₂O, HNO₃ (Acid/Cat. = 50), 80 °C}.

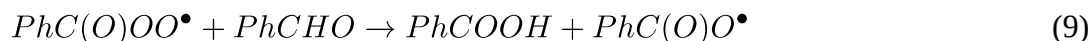
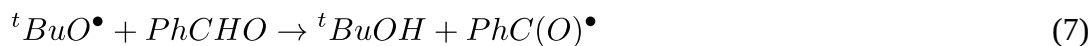
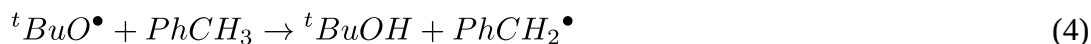
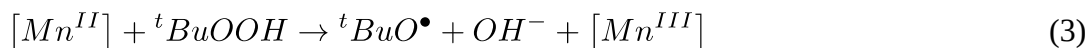
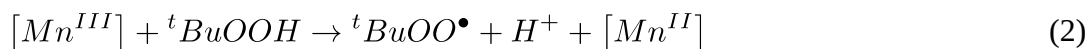
The utilization of the Mn salt precursor used in the synthesis of compound **4** as a catalyst for toluene oxidation led to the formation of benzaldehyde and benzyl alcohol with a total yield of only 6.4%, and no benzoic acid was observed (Table 1, entry 19).

Benzoic acid is widely prevalent and has found applications in diverse production processes. It is commonly employed as a flavoring agent in food, is a component in cosmetics, hygiene, and pharmaceutical products, and serves as an effective preservative with antifungal and antibacterial properties. (65,66)

Based on the optimization study and the significance of benzoic acid as the most desired product, (65,66) performing the toluene oxidation reaction in acetonitrile using 0.5 mol % catalyst **4**, 3 equiv of the TBHP oxidant, and the nitric acid promoter with an acid-to-catalyst molar ratio of 30, under microwave irradiation at 100 °C, resulted in a 36.8% yield of benzoic acid and a total yield of 53.6% after 6 h (Table 1, entry 20).

Performing the reaction in the presence of a carbon- and oxygen-based radical trap, namely, diphenylamine, (**72**) had a significant inhibition effect (Table 1, entry 21), which indicates the

radical nature of the reaction. Therefore, the course of the reaction is expected to follow the mechanism presented in eqs 2–9.



The reaction begins with the metal-assisted decomposition of TBHP (eq 2 and 3), leading to the generation of ${}^tBuOO\bullet$ and ${}^tBuO\bullet$ radicals by reducing Mn(III) or oxidizing Mn(II). (105) The ${}^tBuO\bullet$ radical abstracts a H atom from toluene, forming the benzyl ($PhCH_2\bullet$) radical (eq 4). (106) Subsequently, the benzyl radical reacts with O_2 to yield the benzyl peroxy ($PhCH_2OO\bullet$) radical (eq 5). (107) Through dismutation, the benzyl peroxy radical transforms into benzaldehyde and benzyl alcohol (eq 6). (71–73) The H-abstraction from benzaldehyde by ${}^tBuO\bullet$ results in the formation of the benzoyl ($PhC(O)\bullet$) radical, which in turn reacts with O_2 to obtain the benzoylperoxy ($PhC(O)OO\bullet$) radical (eq 8). This benzoylperoxy radical adds to the carbonyl group of benzaldehyde, forming an adduct that rearranges and fragments into benzoic acid and a benzoyloxy radical (eq 9). (108)

While the catalytic oxidation of toluene using heterogeneous manganese oxide catalysts has been intensively studied, (109–111) the utilization of manganese complexes as homogeneous catalysts remains scarce. In this study, complex **4** was employed as a homogeneous catalyst for toluene oxidation with TBHP in the presence of a nitric acid promoter, which resulted in the formation of benzaldehyde, benzyl alcohol, and benzoic acid as the main products. The catalytic system achieved

a total yield of 53.6%, with a higher selectivity toward benzoic acid (approximately 70%) at 100 °C under microwave irradiation after 6 h.

The utilization of a Mn^{III}–Salen complex as a catalyst for the oxidation of toluene with TBHP, in the presence of the nitric acid promoter, resulted in the formation of benzaldehyde and benzyl alcohol with a total yield of around 6% after 24 h, at room temperature, with a higher selectivity (98%) toward the former product. Complexes based on other transition metals, namely, V, (72,112,113) Cr, (73) Cu, (71) and Au, (114) have been studied as homogeneous catalysts for peroxidative oxidation of toluene in acetonitrile to obtain mixtures of oxygenated products (Table S2). In general, they exhibited moderate activities and a high selectivity toward benzaldehyde formation. In this context, our catalytic protocol demonstrated an enhanced activity in terms of a relatively high total yield of 53.6% and a higher selectivity toward benzoic acid formation.

Conclusions

A convenient acetone-involved approach for cage-like manganesephenylsilsesquioxanes has been developed. This allowed the description of a family of tri and tetra manganese silsesquioxane complexes with different *N,N*-ligands (1,10-phenanthroline, pyrazine, or dmpzH). Application of acetone as a key solvate gave optimistic results in terms of both isolation of early unknown CLMS types and their high yields. Interaction of Mn(III) ions in the pyrazine- and dmpzH-based Mn₃Na₃ compounds resulted in antiferromagnetic behavior. The precatalytic activity of complex **4**, as a representative Mn₃Na₃-based compound, for the oxidation of an aromatic VOC was assessed by using toluene as a model substrate. In this context, complex **4** exhibits a promising catalytic activity toward peroxidation of toluene using the TBHP oxidant in the presence of a nitric acid promoter. The reaction yielded benzaldehyde, benzyl alcohol, and benzoic acid as the primary products, with a relatively high total yield and a high selectivity toward benzoic acid formation under microwave irradiation. The catalytic protocol developed in this study demonstrated enhanced activity toward toluene oxidation when compared to the previously reported homogeneous catalytic systems, which exemplify the effectiveness of the Mn–CLMS catalysts in promoting VOC oxidation reactions toward the formation of value-added organic products.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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